Concentrations of Brominated Flame Retardants (BFRs) in Air and Dust from UK Cars - Spatial Variability and Evidence for Degradation

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Introduction

Whilst evidence mounts of the contamination of indoor air and dust with BFRs and its influence on human body burdens (Roosens et al, 2009; Wu et al, 2007), data pertaining to such contamination of cars remains sparse. However, the limited data available suggest that cars may constitute one of the most contaminated microenvironment categories – for example BDE-209 was present in one UK car dust sample at 0.26% (Harrad et al, 2008). In the two studies to date of airborne BFRs in cars; while one sampled air in the passenger cabin (Mandalakis et al, 2008), the other – for practical reasons – sampled in the trunk (Harrad et al, 2006). We hypothesise that air circulation within vehicles means that concentrations of BFRs in air in the trunk are not significantly different to those in cabin air, and hence trunk air reflects that to which car occupants are exposed in the passenger cabin. Also of interest is the potential for photolytic degradation of BFRs present in air and dust. We have reported previously on the photolytic dehydrobromination of hexabromocyclododecane (HBCD) in indoor dust (Harrad et al, 2009), and of the photolytic debromination of BDE-209 in a sample of car dust (Abdallah et al, 2009). We hypothesise such degradation to be more facile in cars, given the "greenhouse" like conditions within vehicle cabins. To evaluate our hypotheses, we report here a study of PBDEs, HBCDs, HBCD degradation products, and TBBP-A in air and dust in vehicles. We sampled air simultaneously in the passenger cabin and the trunk of 20 cars, and sampled dust from within the cabin and the trunk of 14 cars. To sample air, we deployed a novel passive sampler that allows the collection of both the particulate and vapour phase. This is essential if higher molecular weight BFRs like BDE-209 are to be monitored passively.

Materials and Methods

Air Sampling

Passive air samplers were deployed during 2009 for typically 28 d simultaneously in the passenger cabin and trunk of 20 cars in the West Midlands of the UK – in one car, sampling was not possible in the trunk. The samplers consisted of two sampling media: a PUF disk (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g cm^{-3} density, PACS, Leicester, UK) and a glass fibre filter (GFF, 12.5 cm diameter, 1 μm pore size, Whatman, UK) used for sampling vapour and particulate phase BFRs respectively. The sampling media were fully sheltered between two different size stainless steel housings (18 cm, one L bottom housing and 23 cm, two L top housing). To minimise gravitational deposition of particles, the PUF disk was mounted at the top of the shelter with only the downward face exposed to air. The GFF was suspended in the middle of the sampler housing supported by a stainless steel thin wire mesh disk ((3 mm aperture size, 12.5 cm diameter) mounted on the central screw to collect particulates.

Dust sampling

Dust samples were collected during 2009 from both the passenger cabins and trunks in 14 cars in the West Midlands of the UK. Samples were collected using a portable vacuum cleaner, to which a sock with a 25 µm mesh size (Allied Filter Fabrics Ltd, Australia) was inserted into the nozzle of the device to retain the dust. The socks containing the samples were placed in resealable polyethylene bags for transportation to the laboratory for analysis. Prior to extraction, samples were sieved through a 500 µm mesh and stored in the dark at 4ºC until extraction.

Analysis

Details of the methods used for extraction, clean up and LC-APPI-MS/MS analysis of PBDEs and their accuracy and reproducibility are described elsewhere (Abdallah et al, 2009). Likewise, details of our methods for the determination of HBCDs and their pentabromocyclodecene (PBCD) and tetrabromocyclododecadiene (TBCD) degradation products via LC-MS/MS have been reported previously (Abdallah et al, 2008a).

Results and Discussion

BFR concentrations in vehicle air Table 1 lists concentrations of BFRs detected in air in both the passenger cabin and trunk. To our knowledge, this is the first study to report on concentrations of HBCDs and TBBP-A in vehicle air. BDEs 209, 47 and 99 were the most abundant congeners contributing on average, 6.1, 5.7 and 77.9% respectively to ∑BDEs. This is generally in agreement with previous findings for Greek cars (Mandalakis et al, 2008) where the high levels of BDE 209 in air from cars were considered indicative of emissions from Deca-BDE treated materials. However, concentrations of ∑BDEs (consisting mainly of BDE-209) reported in this study are significantly ($p<0.05$) higher than those reported in cars from Greece (0.4-2644; median = 201 pg m^{-3}) (Mandalakis et al, 2008). This is in agreement with the substantially higher levels of BDE-209 in UK indoor dust (including from cars) compared to other European countries (Harrad et al, 2008) and may be attributed to the fact that due to strict regulations on flame retardancy for domestic upholstery fabrics; the UK has a disproportionately large share of the EU market for DecaBDE. ∑tri-to hexa-BDE concentrations in this study (19-1745; median 133 pg m^{-3}) are generally in line with those reported previously in cars from Birmingham, UK (11-8184; median 41 pg m^{-3}) (Harrad et al, 2006).

Within-vehicle spatial variability in vehicle air As shown in Table 1, paired t-test comparison of concentrations in the cabin and trunk in the same vehicles, revealed no statistically significant ($p<0.05$) differences between HBCD diastereomer profiles or concentrations between trunk and cabin. Likewise, concentrations of both tri through octa-BDEs in cabins and trunks were statistically indistinguishable ($p<0.05$). In contrast, statistical analysis revealed airborne concentrations of TBBP-A and of BDEs 206, 207, 208, and 209 in trunks to be significantly lower ($p<0.05$) than those in cabins.

BFR concentrations in vehicle dust Table 1 lists concentrations of BFRs detected in dust from both the passenger cabin and trunk. Concentrations are in line with previous reports for vehicle dust in both the UK (Abdallah et al, 2008b; Harrad et al, 2008) and the USA (Lagalante et al, 2009).

Within-vehicle spatial variability in vehicle dust Table 1 reveals concentrations of HBCDs, TBBP-A, and BDEs 196, 197, 202, 203, 206, 207, 208, and 209 to be significantly higher ($p<0.05$) in cabin dust than in dust sampled from the trunk. Concentrations of BDEs 47, 85, 99, 100, 153, and 183 were

noticeably higher in cabin dust than in trunk dust, but the difference was not statistically significant ($p>0.05$).

Evidence for BFR photodegradation Table 1 shows there to be a statistically significant excess of the HBCD degradation products PBCDs and TBCDs in cabin as opposed to trunk dust. While this may be simply a reflection of the lower concentrations of the parent HBCDs in trunk dust; it is not inconsistent with enhanced photolytic dehydrobromination of HBCDs in the cabin. Also of note are the significantly higher concentrations of BDE-202 and the higher relative abundance of BDE-208 relative to BDE-209 in cabin dust. BDE-202 has not been identified in any commercial formulation and has been reported to arise from the photodegradation in house dust of BDE-209 (Stapleton and Dodder, 2008). Moreover, the percentage ratio of BDE-208:BDE-209 in commercial formulations does not exceed 0.08% (La Guardia et al, 2008). This is exceeded substantially in cabin dust and to a lesser extent in trunk dust. Combined, these factors suggest strongly that the higher solar irradiance to which BFRs in cabin dust are exposed leads to photodebromination of BDE-209.

Conclusions This study demonstrates that sampling air in car trunks does provide an accurate measure of the concentrations of HBCDs and of tri-to-octa-BDEs to which car occupants are exposed. In contrast, concentrations of TBBP-A and of BDEs 206, 207, 208, and 209 in trunks are significantly lower in cabins. Likewise, sampling trunk dust underestimates significantly concentrations of all target BFRs except for tri-hepta-BDEs, and therefore sampling dust in passenger cabins is essential for the purposes of accurate exposure assessment. Evidence is also provided that photodegradation of HBCDs and BDE-209 is substantial in vehicle cabins.

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References

Abdallah MA, Ibarra C, Harrad S, Neels H, Covaci A. 2008a. J Chrom A 1190:333.

Abdallah MA, Harrad S, Covaci A. 2008b. Environ Sci Technol 42:6855.

Abdallah MA, Harrad S, Covaci A. 2009. Anal Chem 81:7460.

Harrad S, Hazrati S, Ibarra C. 2006. Environ Sci Technol 40:4633.

Harrad S, Ibarra, C, Abdallah MA, Boon R, Neels H, Covaci A. 2008. Environ Int 34:1170.

Harrad S, Abdallah MA, Covaci A. 2009. Environ Int 35:573.

Lagalante AF, Oswald TD, Calvosa FC. 2009. Environ Int 5:539.

La Guardia MJ, Hale RC, Harvey E. 2006. Environ Sci Technol 40:6247.

Mandalakis M, Stephanou EG, Horii Y, Kannan K. 2008. Environ Sci Technol 42:6431.

Roosens L, Abdallah M, Harrad S, Neels H, Covaci A. 2009. Environ Hlth Persp 117:1707.

Stapleton HM, Dodder NG. 2008. Environ Toxicol Chem 27:306.

Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, Webster TF. 2007. Environ Sci Technol 41:1584.

Table 1: Summary of concentrations of target BFRs in air (pg m^{-3}) and dust (ng g^{-1}) from cars

	Cabins (n=20; n=14 for dust)		Trunks (n=19; n=14 for dust)	
BFR	**Median (Air)**	**Median (Dust)**	**Median (Air)**	**Median (Dust)**
α-HBCD	87	***3000***	94	***280***
β-HBCD	39	***1100***	46	***130***
γ-HBCD	250	***9200***	220	***860***
ΣPBCDs	*nm*	***81***	*nm*	***5.0***
ΣTBCDs	*nm*	***15.5***	*nm*	***<LOQ***
TBBP-A	***3***	***4.5***	***1***	***<LOQ***
BDE-47	56	100	63	26
BDE-85	<LOQ	2.5	7	0.35
BDE-99	51	130	61	50
BDE-100	7	17	8	6.5
BDE-153	11	14	18	6.5
BDE-154	<LOQ	10	11	1.5
BDE-183	15	6.0	18	1.5
BDE-196	<LOQ	***41***	<LOQ	***14***
BDE-197	<LOQ	***7.0***	<LOQ	***<LOQ***
BDE-202	*nm*	***14***	*nm*	***0.3***
BDE-203	<LOQ	***16***	<LOQ	***4.0***
BDE-206	***22***	***4800***	***15***	***51***
BDE-207	***17***	***3700***	***9***	***30***
BDE-208	***13***	***4100***	***<LOQ***	***7.0***
BDE-209	***1300***	***190000***	***910***	***2700***
%BDE-208:BDE-209	*nc*	***2.1***	*nc*	***0.3***

Numbers in bold italics indicate a significant difference indicated by paired t-test comparison ($p<0.05$)
nm denotes not measured; nc denotes not calculated; <LOQ denotes below limit of quantitation